

## PATENT COOPERATION TREATY

PCT

## NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Assistant Commissioner for Patents  
United States Patent and Trademark  
Office  
Box PCT  
Washington, D.C.20231  
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

<b>Date of mailing (day/month/year)</b> 24 May 2000 (24.05.00)	
<b>International application No.</b> PCT/US99/21174	<b>Applicant's or agent's file reference</b>
<b>International filing date (day/month/year)</b> 13 September 1999 (13.09.99)	<b>Priority date (day/month/year)</b> 14 September 1998 (14.09.98)
<b>Applicant</b> VORONOV, Oleg, A. et al	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:  
10 April 2000 (10.04.00)

☐ in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was

☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

<b>The International Bureau of WIPO</b> 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35	<b>Authorized officer</b> Diana Nissen Telephone No.: (41-22) 338.83.38
--	---

# PATENT COOPERATION TREATY

## PCT

### INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

REC'D 11 JAN 2001

WIPO

PCT

Applicant's or agent's file reference 99-04	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/US99/21174	International filing date (day/month/year) 13 SEPTEMBER 1999	Priority date (day/month/year) 14 SEPTEMBER 1998
International Patent Classification (IPC) or national classification and IPC IPC(7): C01B 31/02, 31/06; B01J 3/06 and US Cl.: 423/445B, 446, 445R		
Applicant DIAMOND MATERIALS INC.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 4 sheets.
 

☒ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority. (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 4 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of report with regard to novelty, inventive step or industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

Date of submission of the demand  10 APRIL 2000	Date of completion of this report  07 NOVEMBER 2000
Name and mailing address of the IPEA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	Authorized officer  STUART HENDRICKSON
Facsimile No. (703) 305-3230	Telephone No. (703) 308-0651

Jean Proctor  
 Paralegal Specialist

## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/US99/21174

## I. Basis of the report

## 1. With regard to the elements of the international application:\*

☐ the international application as originally filed☒ the description:

pages (See Attached) \_\_\_\_\_, as originally filed  
pages \_\_\_\_\_, filed with the demand  
pages \_\_\_\_\_, filed with the letter of \_\_\_\_\_

☒ the claims:

pages (See Attached) \_\_\_\_\_, as originally filed  
pages \_\_\_\_\_, as amended (together with any statement) under Article 19  
pages \_\_\_\_\_, filed with the demand  
pages \_\_\_\_\_, filed with the letter of \_\_\_\_\_

☒ the drawings:

pages (See Attached) \_\_\_\_\_, as originally filed  
pages \_\_\_\_\_, filed with the demand  
pages \_\_\_\_\_, filed with the letter of \_\_\_\_\_

☒ the sequence listing part of the description:

pages (See Attached) \_\_\_\_\_, as originally filed  
pages \_\_\_\_\_, filed with the demand  
pages \_\_\_\_\_, filed with the letter of \_\_\_\_\_

## 2. With regard to the language, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language \_\_\_\_\_ which is:

☐ the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).☐ the language of publication of the international application (under Rule 48.3(b)).☐ the language of the translation furnished for the purposes of international preliminary examination (under Rules 55.2 and/or 55.3).

## 3. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

☐ contained in the international application in printed form.☐ filed together with the international application in computer readable form.☐ furnished subsequently to this Authority in written form.☐ furnished subsequently to this Authority in computer readable form.☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.4. ☒ The amendments have resulted in the cancellation of:☒ the description, pages NONE☒ the claims, Nos. NONE☒ the drawings, sheets/fig. NONE5. ☐ This report has been drawn as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).\*\*

\* Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).

\*\*Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.

## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/US99/21174

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

## 1. statement

Novelty (N)	Claims <u>1-19</u>	YES
	Claims <u>NONE</u>	NO
Inventive Step (IS)	Claims <u>1-19</u>	YES
	Claims <u>NONE</u>	NO
Industrial Applicability (IA)	Claims <u>1-19</u>	YES
	Claims <u>NONE</u>	NO

## 2. citations and explanations (Rule 70.7)

Claims 1-19 meet the criteria set out in PCT Article 33(4), because the process has applicability to make hard composite materials.

Claims 1-19 meet the criteria set out in PCT Article 33(2)-(3), because the prior art does not teach or fairly suggest the intermediate density or processing steps.

----- NEW CITATIONS -----  
NONE

**Supplemental Box**

(To be used when the space in any of the preceding boxes is not sufficient)

Continuation of: Boxes I - VIII

Sheet 10

**I. BASIS OF REPORT:**

This report has been drawn on the basis of the description,  
page(s) 1-15, as originally filed.  
page(s) NONE, filed with the demand.  
and additional amendments:  
NONE

This report has been drawn on the basis of the claims,  
page(s) NONE, as originally filed.  
page(s) NONE, as amended under Article 19.  
page(s) NONE, filed with the demand.  
and additional amendments:  
Pages 16-19, filed with the letter of 01 September 2000.

This report has been drawn on the basis of the drawings,  
page(s) NONE, as originally filed.  
page(s) NONE, filed with the demand.  
and additional amendments:  
NONE

This report has been drawn on the basis of the sequence listing part of the description:  
page(s) NONE, as originally filed.  
pages(s) NONE, filed with the demand.  
and additional amendments:  
NONE

What is Claimed is:

1. A carbon material formed by the process of:
  - a) providing a fullerene based carbon powder,
  - b) subjecting said fullerene based carbon powder to a pressure of 1.0 to 10:0
- 5 Gpa, a temperature of from 300-1000°C for a period of time from 1 to 10000 seconds.
2. The carbon material as claimed in claim 1, wherein the fullerene based powder comprises at least 99% buckyballs.
3. The carbon material as claimed in claim 1, wherein the fullerene based powder
- 10 comprises at least 99% single walled nanotubes.
4. The carbon material as claimed in claim 1, wherein the fullerene based powder comprises at least 99.9% fullerenes.
5. The carbon material as claimed in claim 1, wherein the pressure is at least 2.5 GPa, the temperature is at least 500°C, and the period of time is at least 1000
- 15 seconds.
6. The carbon material as claimed in claim 1, wherein the fullerene based powder comprises 0.0001 to 1.0% of a dopant.

7. The carbon material as claimed in claim 6, wherein the dopant is selected from the group consisting of hydrogen, boron, nitrogen, oxygen, sulphur, fluorine, and chlorine.

5 8. A process for forming a hard sintered conductive carbon material, comprising the steps of:

- a) providing an fullerene based carbon powder having at least 99% fullerenes,
- b) agglomerating said fullerene based carbon powder;
- c) subjecting said fullerene based carbon powder to pressure of 1.0 to 10.0 Gpa, a temperature of from 300-1000°C for a period of time of from 1 to 10000 seconds.

10 9. The process as claimed in claim 8, wherein the fullerene based powder comprises at least 99.9% by weight of single walled nanotubes.

10. The process as claimed in claim 8, wherein the fullerene based powder comprises at least 99.9% by weight of buckyballs.

15 11. The process as claimed in claim 10, further including the steps of d) providing an alloy used to convert carbon materials to diamond and e) subjecting said sintered carbon material to a pressure of 7.0 to 9.0 Gpa, a temperature of from 800-1300°C for a period of time from 0.1 to 100 seconds to convert the sintered carbon material to polycrystalline diamond.

12. The process as claimed in claim 11, wherein the alloys are based on at least

one of Ni, Fe and Co.

13. The process as claimed in claim 10, further including the steps of d) providing a metal alloy selected from the group comprising aluminum, magnesium and calcium alloys and e) subjecting said sintered carbon material to a pressure of 2.5 to 9.0 —  
5 Gpa, a temperature of from 400-1300°C for a period of time from 10 to 1000 seconds to convert the sintered carbon material to monocrystalline diamond.

14. The process as claimed in claim 8, further including the steps of infiltrating said fullerenes by superplastic flow under temperature and pressure into a porous composite material and said subjecting step takes place after said fullerene based  
10 carbon powder has been infiltrated into the porous material.

15. The process as claimed in claim 14, wherein the superplastic flow takes place at temperatures of 200-400°C at pressures of 0.1-1.0 Gpa.

16. The process as claimed in claim 8, wherein the fullerene based carbon powder comprises 0.0001 to 1.0% of a dopant.

15 17. A conductive carbon material comprising fullerenes subjected to heat, temperature and pressure sufficient to provide a hardness to the material of at least 1.0 Gpa and a resistivity of less than 10 ohms-cm.

18. The process as claimed in claim 17, wherein the fullerenes comprise at least



99.9% by weight of single walled nanotubes.

19. The process as claimed in claim 17, wherein the fullerenes comprise at least 99.9% by weight of buckyballs.

09/787015-

JG08 Rec'd PCT/PTO 12 MAR 2001

IN THE PCT OFFICE

International Application No: **PCT/US99/21174**

Filed: **13 September 1999**

Authorized Officer : **Stuart Hendrickson**

Atty. Docket: **99-04**

**IPEA/US**

Commissioner of Patents and Trademarks  
Box PCT  
Washington, D.C. 20231

REPLY TO WRITTEN OPINION

---

CERTIFICATE OF FACSIMILE TRANSMISSION

I hereby certify that this correspondence is being facsimile transmitted to the Patent and Trademark Office (Fax No. 703 305 3230) on September 1, 2000.

William L. Botjer \_\_\_\_\_  
Typed Name

By   
(Signature)

## REMARKS

Based on the remarks to follow, reconsideration of this application is respectfully requested.

This paper is responsive to the written opinion dated August 1, 2000. In the written opinion claims 1-10 and 16-19 were stated as lacking novelty with respect to the papers to Kozlov and/or Zhang. Claims 1-13 and 16-19 were stated as lacking an inventive step over the same references. Claims 14 and 15 were found to meet the criteria of PCT Article 33(3), applicants gratefully acknowledge this notification.

In response to the written opinion replacement pages 16-19 are herewith submitted to amend independent claims 1, 8 and 17 to more particularly point out and distinctly claim the invention. The changes to claim 1, 8 and 17 are as follows with brackets showing deleted words and underlining showing added wording:

1. A hard carbon material having a density greater than 2.3 g/cm<sup>3</sup> formed by the process of:

a) providing a fullerene based carbon powder,

b) agglomerating said fullerene based carbon powder to a density above 1.4 g/cm<sup>3</sup>.

c) [b)] subjecting said fullerene based carbon powder to a pressure of 1.0 to 10.0 Gpa, a temperature of from 300-1000°C for a period of time from 1 to 10000 seconds.

8. A process for forming a hard high density sintered conductive carbon material, comprising the steps of:

a) providing an fullerene based carbon powder having at least 99% fullerenes,

b) agglomerating said fullerene based carbon powder to a density above 1.4 g/cm<sup>3</sup>;

c) subjecting said fullerene based carbon powder to pressure of 1.0 to 10.0 Gpa, a temperature of from 300-1000°C for a period of time of from 1 to 10000 seconds.

17. A conductive hard, high density carbon material comprising fullerenes subjected to heat, temperature and pressure sufficient to provide a hardness to the material of at least 1.0 Gpa and a resistivity of less than 10 ohms-cm and a density above 2.3 g/cm<sup>3</sup>.

Turning now to the rejections as to novelty and inventive step, for the reasons set forth in detail below it is respectfully submitted that the invention set forth in the claims as amended are novel and provide an inventive step over the art of record, when taken alone or in combination. The present invention is directed to a new hard dense carbon material (and the method of making it) that is an amorphous carbon ceramic (unlike graphite or graphite-like ceramics and unlike diamond or diamond-like ceramics). This material is formed by agglomerating, pressing and heating of fullerene based carbon powder. The resultant carbon material is harder and denser than graphite and softer than diamond or almost as hard as diamond, depending on the pressing and heating parameters. This carbon material is conductive like graphite and unlike diamond, which is an insulator.). As is discussed in detail below, neither of the cited references, Kozlov and Zhang, achieves the hard dense carbon material of the present invention.

The paper to Kozlov is directed to the formation of "superhard" but low density form of carbon from C<sub>60</sub> fullerenes as the final density of the material formed by Kozlov is about 1.9 g/cm<sup>3</sup> (see the final paragraph on page 1199 of the Kozlov

paper) which is barely more than the starting density of  $1.7 \text{ g/cm}^3$ , which is less than half of the density of diamond and which is even less dense than graphite. In contrast the density of the carbon material formed in the present application is 2.3-3.0  $\text{g/cm}^3$  (see Table 2 of the present application) and claims 1, 8 and 17 have been amended to recite this greater density. Accordingly, the material defined in claims 1 and 17 is distinct in its physical properties from that of Kozlov. As the process of Kozlov is not well discussed in the paper it is clear that the best test of the differences is the resulting product, in this case it is manifest that both the process (claim 8) and the product of the present application is distinct from that of Kozlov.

Regarding the dependent claims and Kozlov, it is noted that Kozlov teaches nothing with respect to the use of nanotubes, single walled or otherwise, as a starting material (present claims 3,9 and 18); does not quantify the purity of the starting materials (claims 2, 3, 4, 9, 10, 18 and 19)-although Kozlov's material evidently was contaminated with aluminum (see the last sentence on page 1199 of the Kozlov paper) ; does not teach the use of a dopant (claims 6, 7 and 16); and does not teach further processing steps to produce diamond (claims 11, 12, and 13). Accordingly the material and methodology defined in the dependent claims are patentable over Kozlov for the reasons set forth above with respect to the independent claims as well as for the additional recitations set forth in the dependent claims.

The short paper to Ma teaches the manufacture of diamonds from fullerenes but does not do so in the context of the manufacture of the amorphous hard high density carbon material of the present application.

In the written opinion it is stated that the Zhang paper teaches treating carbon

nanotubes under high pressure and temperature to make "a hard material". It is respectfully submitted that there is no teaching in Zhang that the material produced is hard. Indeed Zhang appears to produce nothing more than graphite which is quite soft (see the upper paragraph, right hand column on page 1672 of the Zhang paper). There also no teaching as to the density of the finished material. The Zhang paper appears to be simply a research paper on the effect of high pressure and temperature on carbon nanotubes which transformed the nanotubes into graphite, hardly an economic process. Thus it is seen that Zhang actually "teaches away" from the work of present application in that its process produces nothing more than graphite instead of the conductive hard, high density carbon material of the present application. A teaching away from the current development is a hallmark of an inventive step.

Regarding the dependent claims and Zhang it is noted that Zhang teaches nothing with respect to the use of buckyballs rather than nanotubes (present claims 2, 10 and 19); does not state whether the nanotubes are single walled (present claims 3,9 and 18); does not quantify the purity of the starting materials as being above 99% (claims 2, 3, 4, 9, 10, 18 and 19)- Zhang's material was only 90% pure (see the second full paragraph on page 1672 of the Zhang paper); does not teach the use of a dopant (claims 6, 7 and 16); and does not teach further processing steps to produce diamond (claims 11, 12, and 13). Accordingly the material and methodology defined in the dependent claims are patentable over Zhang for the reasons set forth above with respect to the independent claims as well as for the additional recitations set forth in the dependent claims.

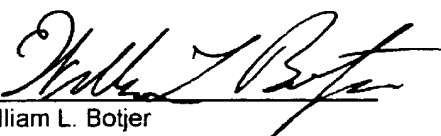
In conclusion, we respectfully submit that the fact that none of the applied

references, even if combined, provides the the material of the same physical specifications as that the present invention is proof positive that the subject matter of the present claims would not be obvious to a person skilled in this art.

Accordingly, we believe that the claims as amended are novel and define an inventive step over the prior art when taken alone or in combination.

It is believed that this response has attended to the matters raised in the Written Opinion and notice to that effect is earnestly solicited. If however, the International Preliminary Examining Authority finds this response insufficient or has any questions regarding this matter, the International Preliminary Examining Authority is requested to telephone applicants attorney at the number listed below prior to issuing a further Opinion.

Dated: September 1, 2000

By   
William L. Botjer  
Reg. No. 27,990  
PO Box 478  
Center Moriches, NY 11934  
(212) 737-5728 (Tue-Thurs)  
(631) 874-4826 (Mon & Fri)

EE227217307US

What is Claimed is:

1. A hard carbon material having a density greater than  $2.3 \text{ g/cm}^3$  formed by the process of:
  - a) providing a fullerene based carbon powder,
  - b) agglomerating said fullerene based carbon powder to a density above  $1.4 \text{ g/cm}^3$ ;
  - c) subjecting said fullerene based carbon powder to a pressure of 1.0 to 10.0 Gpa, a temperature of from  $300\text{-}1000^\circ\text{C}$  for a period of time from 1 to 10000 seconds.
2. The carbon material as claimed in claim 1, wherein the fullerene based powder comprises at least 99% buckyballs.
3. The carbon material as claimed in claim 1, wherein the fullerene based powder comprises at least 99% single walled nanotubes.
4. The carbon material as claimed in claim 1, wherein the fullerene based powder comprises at least 99.9% fullerenes.
5. The carbon material as claimed in claim 1, wherein the pressure is at least 2.5 GPa, the temperature is at least  $500^\circ\text{C}$ , and the period of time is at least 1000 seconds.



EE227217307US

6. The carbon material as claimed in claim 1, wherein the fullerene based powder comprises 0.0001 to 1.0% of a dopant.

7. The carbon material as claimed in claim 6, wherein the dopant is selected from the group consisting of hydrogen, boron, nitrogen, oxygen, sulphur, fluorine, and chlorine.

8. A process for forming a hard high density sintered conductive carbon material, comprising the steps of:

a) providing an fullerene based carbon powder having at least 99% fullerenes,

b) agglomerating said fullerene based carbon powder to a density above 1.4 g/cm<sup>3</sup>;

c) subjecting said fullerene based carbon powder to pressure of 1.0 to 10.0 Gpa, a temperature of from 300-1000°C for a period of time of from 1 to 10000 seconds.

9. The process as claimed in claim 8, wherein the fullerene based powder comprises at least 99.9% by weight of single walled nanotubes.

10. The process as claimed in claim 8, wherein the fullerene based powder comprises at least 99.9% by weight of buckyballs.



11. The process as claimed in claim 10, further including the steps of d) providing an alloy used to convert carbon materials to diamond and e) subjecting said sintered carbon material to a pressure of 7.0 to 9.0 Gpa, a temperature of from 800-1300°C for a period of time from 0.1 to 100 seconds to convert the sintered carbon material to polycrystalline diamond.

12. The process as claimed in claim 11, wherein the alloys are based on at least one of Ni, Fe and Co.

13. The process as claimed in claim 10, further including the steps of d) providing a metal alloy selected from the group comprising aluminum, magnesium and calcium alloys and e) subjecting said sintered carbon material to a pressure of 2.5 to 9.0 Gpa, a temperature of from 400-1300°C for a period of time from 10 to 1000 seconds to convert the sintered carbon material to monocrystalline diamond.

14. The process as claimed in claim 8, further including the steps of infiltrating said fullerenes by superplastic flow under temperature and pressure into a porous composite material and said subjecting step takes place after said fullerene based carbon powder has been infiltrated into the porous material.

15. The process as claimed in claim 14, wherein the superplastic flow takes place at temperatures of 200-400°C at pressures of 0.1-1.0 Gpa.

16. The process as claimed in claim 8, wherein the fullerene based carbon powder

comprises 0.0001 to 1.0% of a dopant.

17. A conductive hard, high density carbon material comprising fullerenes subjected to heat, temperature and pressure sufficient to provide a hardness to the material of at least 1.0 Gpa and a resistivity of less than 10 ohms-cm and a density above 2.3 g/cm<sup>3</sup>.

18. The process as claimed in claim 17, wherein the fullerenes comprise at least 99.9% by weight of single walled nanotubes.

19. The process as claimed in claim 17, wherein the fullerenes comprise at least 99.9% by weight of buckyballs.



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>7</sup> :</b> <b>C01B</b>	<b>A2</b>	<b>(11) International Publication Number:</b> <b>WO 00/15548</b> <b>(43) International Publication Date:</b> 23 March 2000 (23.03.00)
<b>(21) International Application Number:</b> PCT/US99/21174 <b>(22) International Filing Date:</b> 13 September 1999 (13.09.99)  <b>(30) Priority Data:</b> 60/100,078 14 September 1998 (14.09.98) US  <b>(71) Applicant (for all designated States except US):</b> DIAMOND MATERIALS INC. [US/US]; 120 Centennial Avenue, Piscataway, NJ 08854-3908 (US).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> VORONOV, Oleg, A. [RU/US]; 56B Cedar Lane, Highland Park, NJ 08904 (US). TOMPA, Gary, S. [US/US]; 43 Franklin Drive, Belle Mead, NJ 08502 (US).  <b>(74) Agent:</b> BOTJER, William, L.; P.O. Box 478, Center Moriches, NY 11934 (US).		<b>(81) Designated States:</b> JP, KR, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>Without international search report and to be republished upon receipt of that report.</i>
<b>(54) Title:</b> FULLERENE BASED SINTERED CARBON MATERIALS  <b>(57) Abstract</b>  A new class of carbon materials and their synthesis. The new carbon materials are formed by high pressure and high temperature processing of fullerene based carbon powder. The new carbon materials are harder than graphite and can be harder than steel (when the starting fullerenes are single wall nanotubes) or almost as hard as diamond (when the starting fullerenes are C <sub>60</sub> buckyballs). The physical attributes of the materials can also be controlled by the pressing and heating parameters. These new carbon materials are conductive like graphite and unlike diamond which is an insulator. The materials can be formed by powder metallurgy techniques into any shape (cylinders, balls, tubes, rods, cones, foils, fibers or others). The new materials can also be readily doped, converted to diamond, formed within a porous composite or converted to diamond within the porous composite.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

## FULLERENE BASED SINTERED CARBON MATERIALS

CROSS REFERENCE TO RELATED APPLICATIONS

This application claims priority of US provisional application S.N. 60/100,078 filed Sept 14, 1998.

5        STATEMENT OF GOVERNMENT SUPPORT OF THE INVENTION

The work resulting in this invention was supported by the Defense Advanced Projects Agency (DARPA). Defense Small Business Innovation Research Program ARPA order No. D611, Amdt 27 issued by U.S.. Army Aviation and Missile Commander under Contract DAAH01-98CR008.

10       BACKGROUND AND SUMMARY OF THE INVENTION

The present application is directed to a new class of carbon materials and their synthesis.

15       The conventional carbon materials are graphite, graphite-like ceramics or diamond and diamond-like ceramics. These materials are produced from carbon-containing compounds: oil, gases, coal, wood, coke, soot, graphite powder, diamond powder, hydrocarbons, polymers or mined as natural minerals. The lattice of graphite consist of planar layers of hexagons, where the carbon atoms have  $sp^2$ -hybridization of the electron shells. The lattice of diamond consists of tetragons,

where the carbon atoms have  $sp^3$ -hybridization of the electron shells. Graphite is a very soft and weak material, with a hardness of 1 on the Mohs scale (1-2 for some graphite-like ceramics), it is conductive, sometimes referred to as a semimetal.

Diamond is an extremely hard and tough material with a Mohs hardness of 10, it is non-conductive, but may be made semiconductive with doping.

Recently, much study has been made of ordered carbon molecules having distinct geometries, such as spheres (known as "buckyballs") and tubular shapes ("nanotubes"), these geometric shapes are generally comprised of relatively large numbers of carbon atoms such as  $C_{60}$ ,  $C_{70}$ ,  $C_{80}$  etc. These ordered carbon molecules are often referred to as "Fullerenes" after the architect Buckminster Fuller, whose geometric designs the molecules resemble. The new carbon materials are synthesized (sintered) using powder metallurgy and/or ceramic pressing techniques from relatively pure amounts of ordered carbon nanoparticles such as  $C_{60}$  buckyballs (which have a spherical icosahedral symmetry) and nanotubes (which can be thought of as a tubular micro-crystal of graphite or a much elongated buckyball with open or closed ends) at high pressures and high temperatures (HPHT).

The new carbon materials are formed by pressing and heating of powder in the form of specially prepared fullerenes. These carbon materials are much harder than graphite and graphite like ceramics and are almost as hard as diamond, depending on the starting fullerenes, the pressing and heating parameters. These new carbon materials are conductive like graphite. The material can be formed by powder metallurgy techniques into any shape (cylinders, balls, tubes, rods, cones, foils, fibers or others). The pressure of compacting is from 1.0-10.0 GPa, the

temperature is 300-1000°C and the period of time is from 1-10000 second. The special carbon soots are: (a) nanotube like, (b) buckyball like, or (c) mixtures of the same with similar diameters (one dimension size) of particles of 0.7-7.0 nm. The particles are pure carbon of 99% or more preferably 99.9+ % (or specially doped by other elements), separated by a narrow range of diameters, for example 0.7-1.0 nm;

The physical properties of the new carbon materials that are produced depend on the type and purity of the starting fullerenes. A strong carbon conductive material is formed by HPHT processing when the starting fullerenes comprise purified single wall nanotubes (or a mixture of single walled nanotubes and buckyballs) which has a hardness (7-9 ½ on the Mohs Scale) greater than that of steel but less than that of silicon carbide (SiC). When the starting fullerenes comprise purified C<sub>60</sub> buckyballs of uniform size an extremely hard (9 ½-10 on the Mohs Scale) conductive amorphous carbon material is formed under HPHT processing which has a hardness greater than that of silicon carbide and which is only slightly less hard than non-conductive diamond or cubic boron nitride. The new carbon materials may be formed within porous ceramic composite "sponges" to form other useful engineering materials by first impregnating the porous ceramic with the appropriate carbon compound and then converting them directly into the new carbon materials.

In particular, the two new carbon materials: 1) nanotube based sintered carbon material and 2) buckyball based sintered carbon material, exhibit hardnesses better than stainless steel (for nanotube based sintered carbon material) and near that of diamond (for buckyball based sintered carbon material). These materials are near isotropic "polymeric" materials, not poly or single



crystalline materials. The polymeric isotropicity is what sets these materials apart—they are extremely tough, greatly resisting fracturing in comparison to c-BN or diamond or other crystals.

Synthesis of the new carbon materials has been demonstrated for millimeter  
5 sized pellets, which allow characterization of mechanical, electrical and other —  
properties that are pertinent to military, industrial and scientific applications. The  
new carbon materials, with their high strength and toughness, may well fulfill the  
need for lightweight engineering materials for military, aerospace, automotive, and  
other industries. Since the materials are conductive, they may also be  
10 superconductive or be made semiconductive, in either case especially with proper  
dopants. It is theorized that the new carbon material is a semimetal and that the new  
carbon material based ceramics may have the metallic and semiconductive type of  
conductivity depending on dopants and parameters of synthesis.

Traditional graphite may be transformed into diamond at pressure of 15 GPa  
15 and temperature of 4000°C. Graphite mixed with metals Ni, Fe, Co or alloys or  
hydrocarbons may be transformed into diamond in the P,T-region of the  
thermodynamical stability of diamond, for example at pressure of 5.5 GPa and  
temperature of 1500°C. Graphite may be transformed into diamond in presence of  
atomic hydrogen and a diamond substrate in the P,T region of the thermodynamical  
20 stability of graphite, for example at low pressure of 0.104 Mpa and a graphite  
substrate temperature of 2000°C (if the temperature of the diamond substrate is  
600-1000°C). Conversely, diamond may be transformed into graphite at pressure of  
0.1 Mpa and temperature of 2000°C. Diamond mixed with metals Ni, Fe, Co or alloys  
may be transformed into graphite in P,T-region of the thermodynamical stability of

graphite, for example at pressure of 0.1 Mpa and temperature of 1000°C in inert gas.

It has also been found that the buckyball based sintered carbon material can be transformed into polycrystalline or monocrystalline diamond at temperatures and pressures less than needed for graphite. Furthermore, the buckyball based sintered carbon material may be transformed into monocrystalline diamond in the presence of alloys that do not catalyze the transformation of graphite into diamond

The new buckyball based sintered carbon material can be used to provide ceramic composite materials. It was found that the smallest particles of carbon soot (buckyball  $C_{60}$ ) have the property of superplasticity in the temperature range of 200-400°C at pressures of 0.01 to at least 1.0 GPa. Graphite, diamond,  $B_4C$ , WC/Co, Cu, Ti, TiC, SiC, Be, W, B, Fe and other porous sponges were prepared by various standard methods and impregnated with carbon soot at a pressure of 1.0 GPa and a temperature of 300°C. The sample then was cooled, the pressure was thereafter increased to 2.5 GPa and the temperature increased to 400°C and held for 1000 sec. The particles of soot were sintered together inside the pores by HPHT treatment to produce composites with a new carbon material matrix which was found to be harder than silicon carbide (30 GPa).

### DESCRIPTION OF THE PREFERRED EMBODIMENTS

For optimum consolidation of the new fullerene based sintered carbon materials it has been important to utilize high purity levels in the starting buckyball and nanotube powders. Generation of fullerenes by the conventional graphite electric arc method yields  $C_{60}$ , a number of higher fullerenes, and other carbonaceous materials such as nanotubes, nanoparticles and insoluble residue (as

a whole, known as soot or carbon black).

Production of fullerene based sintered carbon material generally requires: 1) purification of the starting material into at least 99%, and preferably >99.9%, pure carbon material of either buckyball C<sub>60</sub> or single walled nanotubes 2) agglomeration (compaction) of the purified fullerene powder into a relatively dense material and 3) HPHT processing (sintering) of the purified, compacted fullerenes to produce the fullerene based sintered carbon materials.

Purification of nanotubes from nanotube/nanoparticle mixtures has been tried with standard techniques such as filtration, chromatography, centrifugation of sonicated solution of raw material. Recently the oxidation of nanoparticles at higher temperatures has proved to yield high purity nanotubes. It has been reported that carbon nanotubes are more resistant to oxidation in air than other fullerene derivatives, for example nanotubes oxidize completely at  $\approx 800^{\circ}\text{C}$ , whereas buckyballs require  $\approx 515^{\circ}\text{C}$  for complete oxidation. Alternatively, an iterative process of sublimation and solvent rinses has been used to purify buckyballs and nanotubes.

Previous experience in synthesis of microscopic quantities of buckyball based sintered carbon material from C<sub>60</sub> buckyballs has demonstrated the typical need for long-term treatment of the buckyball powder samples at  $160^{\circ}\text{C}$ – $400^{\circ}\text{C}$  to remove absorbed gases and contaminants of organic compounds. It has been found that sublimed and recondensed agglomerates make the best compaction material because they overcome discrete particle adsorbate contamination and static charging. Of course, if a supplier can achieve sufficient levels of purity and agglomeration, the need to perform these steps is minimized.

Sample preparation and compaction procedures

The following procedures for sample preparation and compaction were used:

The samples were placed in graphite heating elements. As produced  $C_{60}$  buckyball powder contains a lot of admixtures of organic compounds. To purify the raw  $C_{60}$ , –

5 the material was sublimated in a gradient quartz tube inserted into the furnace with one cold end. The tube was connected to a vacuum pump and a helium cylinder.  $C_{60}$  was evaporated at the hot zone of the tube and deposited at the cold end. Organic compounds were mostly removed into the vacuum system in gaseous form. The growth of fullerene grains was observed through the quartz glass. When the size of

10 the crystals was large enough, the cooled part of the tube was disconnected and the grains were poured into a crucible. The grains were then separated by size, (for example 60/40 microns) using sieves and a shaking device, coarse grains up to 1000/800 microns were also used. Such pure fullerene  $C_{60}$  buckyball powder is easily agglomerated by cold pressing in a die at a pressure of 0.05-0.50 GPa. An

15 agglomerated material with density of  $\rho=1.6 \text{ g/cm}^3$  was achieved, which is greater than the density of some types of graphite ceramics ( $\rho=1.5 \text{ g/cm}^3$ ). Utilizing precleaned buckyball and nanotube high purity agglomerates, powders were cold pressed into discs at pressures of 0.05 to 0.5 GPa

The same procedure was tried with multi-wall nano-tubes, however they

20 could not be agglomerated by cold pressing. It is impossible to cold compact this type of carbon black in the examined pressure range, as is also the case for acetylene soot or any other tube or soot, where the particles are not separated properly. The poured density of soot is about  $0.1 \text{ g/cm}^3$ , which is only 2.5% of that of

solid carbon. The density of agglomerated soot is 0.30-0.35 g/cm<sup>3</sup>. Agglomeration of multi-wall nanotubes also gives a density of 0.35-0.40 g/cm<sup>3</sup>. It is possible to achieve such density by agglomerating nanograin diamond-like explosive soot. However, in the phase space examined, such density is not high enough for further sintering under high pressure, and HPHT treatment is not effective. It appears that density of the sintered bulk material depends on the density of the "green body". Thus, the initial powder density is a critical parameter. However, single-wall nanotubes are easily agglomerated by the same method as buckyballs. Cold pressing inside the die at a pressure of 0.05 to 0.5 GPa gives pellets with  $\rho=1.4-1.5$  g/cm<sup>3</sup>.

#### HPHT Consolidation of the Agglomerated Fullerene Powders

The synthesis of man made diamonds has taken place for many years, this synthesis uses high pressure and temperature processing of carbon materials, usually in the presence of metal alloys which act as catalysts. Thus machinery capable of such HPHT processing has also been known for some time, as the temperatures and pressures required for carrying out the steps to produce the fullerene based sintered carbon materials of the present invention are either similar to, or less than, those for man made diamond production, the equipment used in those processes may be used herein. A suitable HPHT apparatus is shown in U.S. Patent No. 3,746,484 to Vereshagin et al entitled "Apparatus for Developing High Pressure and High Temperature" which issued on July 17, 1973; the disclosure of which is hereby incorporated by reference as if fully set forth herein. Other suitable apparatus is shown in U.S. Patent No. 2,941,242 to Hall which issued in June 1960.

It should be noted for processes requiring pressures of less than 5.0 Gpa simpler apparatus can be effectively used.

The HPHT equipment of the above noted Vereshagin et al patent includes a graphite crucible for holding the powders to be processed. An electric current is passed through the crucible which provides the necessary heating. The crucible is held between contoured anvils which are acted upon by a hydraulic press to provide the necessary pressure. In the case at hand the buckyball material was purified and then agglomerated to preferably form 50-100 micron grain size powder, although larger or smaller sizes are also useable. The powder was further agglomerated into pellets by cold pressing. The samples were put into the graphite crucible, which also serves as the heater, and placed in the HPHT apparatus .

A number of samples were prepared from buckyball carbon soot processed as described above, and thereafter subjected to HPHT sintering. In table 1 to follow the sample number is shown in column 1, the pressure used in the HPHT processing is shown in the first column, the pressure is shown in the second column, the temperature is shown in the third column, the time to which the sample is subjected to the temperature and pressure is shown in the fourth column, the hardness of the processed sample is shown in the fifth column and the resistivity of the sample is shown in the sixth column:

**Table 1**

No	P, Gpa	T, °C	t, sec.	H, Gpa	R ohms*cm
1	9.0	400	1000	45	0.006
2	8.0	400	1000	40	0.008
3	7.0	400	1000	38	0.009
4	5.5	400	1000	35	0.0085
5	2.5	400	1000	31	0.04
6	1.0	400	1000	1	10
7	8.0	300	1000	0.1	$>10^{10}$
8	8.0	500	1000	41	0.0075
9	8.0	600	1000	42	0.007
10	8.0	700	1000	43	0.0065
11	8.0	800	1000	43	0.006
12	8.0	900	1000	20	0.005
13	8.0	1000	1000	10	0.003
14	8.0	400	1	1	10
15	8.0	400	10	10	1.0
16	8.0	400	100	25	0.1
17	8.0	400	10000	43	0.007
18	9.0	350	10000	50	0.005

It is also seen that the hardness of the buckyball based sintered carbon material can be controlled by the selection of pressure, temperature and processing time. In summary, the results are: sample hardness grows with pressure, temperature and holding time up to the temperature 800°C, then the hardness decreases. The samples sintered at 200-350°C are usually still soft; samples sintered at 400-800°C are usually hard. The pressure of 2.5 GPa, temperature of 500°C, holding of 1000 sec. are high enough parameters to obtain the samples that scratch monocrystalline SiC, as well as all other materials, excluding cubic boron nitride (c-BN) and diamond. It was found that the conductivity of the samples increases as the hardness increases, the soft samples were good insulators with the

hardest samples having a resistivity of approximately  $10^{-2}$  ohms /cm at ambient temperature and pressure. For single wall nanotube based sintered carbon material the process parameters set forth in Table 1 will produce material of similar properties but with somewhat less hardness, see Table 2 to follow. It may also be possible to utilize pressures less than 1.0 Gpa or greater than 10 Gpa if the other parameters are adjusted to compensate therefore.

Table 2 below compares certain physical properties of the fullerene based sintered carbon materials synthesized herein with other carbon based materials: graphite, diamond and ceramics based thereon. It is seen that the nanotube based sintered carbon material is harder, denser and stronger than graphite and graphite based ceramics while still being conductive. It is seen that the buckyball based sintered carbon material has hardness, density and strength properties which closely approach that of diamond, yet the material is very conductive while diamond is an insulator.

**Table 2**

Material Properties	G	G-Based Ceramics	D	D-Based Ceramics	Bu*	Nt
Density $\rho$ , gm/cm <sup>3</sup>	2.2	1.5-2.1	3.5	3.0-3.4	2.3-3.0	2.3-2.8
Hardness H, Gpa Mohs	0.1 ½-1	0.1-1.0 ½-6	60-100 10	60-75 10	1.0-60 6-10	1.0-30 6-9 ½
Resistivity $\xi$ , $\Omega$ cm	$10^{-5}$ - $10^{-2}$	$10^{-2}$ - $10^{-3}$	$10^{24}$	$10^6$ - $10^{12}$	0.01-10	0.01-10

G-graphite, D-diamond,

Bu-buckyball based sintered carbon material (as sintered at P= 1.0-10.0 GPa)

Nt-nanotube based sintered carbon material (as sintered at P= 1.0-10.0 GPa)

\*typical properties as shown by sample 5.



Theoretical evaluation shows that the compressive strength and density of the buckyball based sintered carbon materials should approach that of diamond which has unsurpassed compressive strength and compressive strength to density ratio.

5            Diamond Creation            —

Buckyball based sintered carbon material may be transformed into polycrystalline diamond more readily than graphite ceramics at pressures of 7.0-9.0 Gpa. Generally, buckyball based sintered carbon material transforms into polycrystalline diamond at lower temperature and for a shorter time in the presence  
10 of Ni-Mn and Ni-Cr alloys than graphite. The temperature of transformation into diamond was 800-1300°C with a holding time of 0.1-100 sec. Transformation usually occurs in 3-4 seconds, some samples were obtained in 1 second, perhaps less. In addition to Ni based alloys, other suitable alloys for creation of polycrystalline diamond are Fe and Co based alloys (Ni-Fe-Co, Ni-Cr, Ni-Fe-Co-Cr  
15 and the like). A mixture with pure Ni transforms with a detonative reaction, so the speed of transformation is higher than the speed of sound in the solid state.

A surprising result is that buckyball based sintered carbon material may be transformed into monocrystalline diamond in the presence of Al-Mg-Ca alloys and other alloys that do not catalyze the transformation of graphite into diamond.  
20 Transformation at  $P=2.5-9.0$  Gpa,  $T=400-1300^{\circ}\text{C}$  and  $t=10-1000$  seconds was studied. The samples were white or white-grey, or black-grey nanograined powders or an amorphous material. White transparent unshaped or cubically shaped with mirror facets, white with black inclusions or black monocrystals of diamond may be easily removed from this powder by tweezers. The size of crystals is 0.1-1 mm at a

holding time of 100 seconds, electron beam diffraction analysis of these samples, demonstrates that they are single crystals of diamond. X-ray analysis of these samples demonstrates that they are pure carbon. They have a hardness of 10 on Mohs scale.

5           Composite Material

The new buckyball based sintered carbon material can be used to provide ceramic composite materials. It was found that the smallest fullerene particles of carbon soot (buckyball C<sub>60</sub>) have the property of superplasticity in the temperature range of 200-400°C at pressures of 0.01-1.0 GPa. Graphite, diamond, B, C, B<sub>4</sub>C, SiC, TiC, WC/Co, Cu, Ti, Fe, Be, W and other ceramic and/or metal porous composite "sponges" were prepared by various standard methods and impregnated with buckyball based carbon soot at a pressure of 1.0 GPa and a temperature of 300°C. The sample then was cooled, the pressure was thereafter increased to 2.5 GPa and the temperature increased to 400°C and held for 1000 sec. The buckyball particles were sintered together inside the pores after the HPHT treatment to produce composites with a new carbon material matrix which was found to be harder than silicon carbide (30 Gpa). When processed into prototype cutting/drilling tool bits, these composites have shown cutting rates comparable to or exceeding those measured for commercially available polycrystalline diamond composites. Further HPHT processing at the parameters and alloys described above for diamond creation can convert the buckyball based sintered carbon material into diamond within the porous matrix.

Doped fullerene based sintered carbon material

The electronic properties of the fullerene based sintered carbon materials can be altered by doping with hydrogen, boron, nitrogen, oxygen, sulphur, fluorine, chlorine, and other elements. Such doping can result in tough new polymers and  
5 new organic compounds as well as providing semiconductivity or superconductivity to the fullerene based sintered carbon materials. As the amount of dopant required is typically 0.0001 to 1.0% by weight. The doping can be achieved by mixing the >99% fullerene powder (either buckyballs or nanotubes) with powders containing a predetermined quantity of the dopants, such as hydrocarbons (for example  
10 naphthalene) or carboranes (for example o-carborane). The fullerene carbon powder and the dopant containing powder are then sintered together.

In summary, a new class of carbon materials is formed by the methodology of the present application. The new carbon materials are formed by high pressure and high temperature processing of fullerene based carbon powder. The new carbon  
15 materials are harder than graphite and either almost as hard as diamond or harder than steel, depending on the starting fullerenes ( $C_{60}$  buckyballs or single wall nanotubes, respectively) as well as the pressing and heating parameters. The new carbon materials are either completely amorphous and isotropic (when formed from buckyballs) or almost completely amorphous and isotropic (when formed from single  
20 wall nanotubes). These new carbon materials are conductive like graphite and unlike diamond which is an insulator. The materials can be shaped by powder metallurgy techniques into any configuration. The new materials can also be readily converted to diamond or formed within a porous composite.

The invention has been described with respect to preferred embodiments. However, as those skilled in the art will recognize, modifications and variations in the specific details which have been described and illustrated may be resorted to without departing from the spirit and scope of the invention as defined in the  
5 appended claims.

What is Claimed is:

1. A carbon material formed by the process of:

a) providing a fullerene based carbon powder,

b) subjecting said fullerene based carbon powder to a pressure of 1.0 to 10.0

5 Gpa, a temperature of from 300-1000°C for a period of time from 1 to 10000 seconds.

2. The carbon material as claimed in claim 1, wherein the fullerene based powder comprises at least 99% buckyballs.

10 3. The carbon material as claimed in claim 1, wherein the fullerene based powder comprises at least 99% single walled nanotubes.

4. The carbon material as claimed in claim 1, wherein the fullerene based powder comprises at least 99.9% fullerenes.

15 5. The carbon material as claimed in claim 1, wherein the pressure is at least 2.5 GPa, the temperature is at least 500°C, and the period of time is at least 1000 seconds.

6. The carbon material as claimed in claim 1, wherein the fullerene based powder comprises 0.0001 to 1.0% of a dopant.

7. The carbon material as claimed in claim 6, wherein the dopant is selected from the group consisting of hydrogen, boron, nitrogen, oxygen, sulphur, fluorine, and chlorine.

8. A process for forming a hard sintered conductive carbon material, comprising the steps of:

- a) providing an fullerene based carbon powder having at least 99% fullerenes,
- b) agglomerating said fullerene based carbon powder;
- c) subjecting said fullerene based carbon powder to pressure of 1.0 to 10.0 Gpa, a temperature of from 300-1000°C for a period of time of from 1 to 10000 seconds.

9. The process as claimed in claim 8, wherein the fullerene based powder comprises at least 99.9% by weight of single walled nanotubes.

10. The process as claimed in claim 8, wherein the fullerene based powder comprises at least 99.9% by weight of buckyballs.

11. The process as claimed in claim 10, further including the steps of d) providing an alloy used to convert carbon materials to diamond and e) subjecting said sintered carbon material to a pressure of 7.0 to 9.0 Gpa, a temperature of from 800-1300°C for a period of time from 0.1 to 100 seconds to convert the sintered carbon material to polycrystalline diamond.

12. The process as claimed in claim 11, wherein the alloys are based on at least

one of Ni, Fe and Co.

13. The process as claimed in claim 10, further including the steps of d) providing a metal alloy selected from the group comprising aluminum, magnesium and calcium alloys and e) subjecting said sintered carbon material to a pressure of 2.5 to 9.0 –  
5 Gpa, a temperature of from 400-1300°C for a period of time from 10 to 1000 seconds to convert the sintered carbon material to monocrystalline diamond.

14. The process as claimed in claim 8, further including the steps of infiltrating said fullerenes by superplastic flow under temperature and pressure into a porous composite material and said subjecting step takes place after said fullerene based  
10 carbon powder has been infiltrated into the porous material.

15. The process as claimed in claim 14, wherein the superplastic flow takes place at temperatures of 200-400°C at pressures of 0.1-1.0 Gpa.

16. The process as claimed in claim 8, wherein the fullerene based carbon powder comprises 0.0001 to 1.0% of a dopant.

15 17. A conductive carbon material comprising fullerenes subjected to heat, temperature and pressure sufficient to provide a hardness to the material of at least 1.0 Gpa and a resistivity of less than 10 ohms-cm.

18. The process as claimed in claim 17, wherein the fullerenes comprise at least

99.9% by weight of single walled nanotubes.

19. The process as claimed in claim 17, wherein the fullerenes comprise at least 99.9% by weight of buckyballs.



PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification<sup>6</sup> :</b> C01B 31/02, 31/06, B01J 3/06	<b>A3</b>	<b>(11) International Publication Number:</b> WO 00/15548 <b>(43) International Publication Date:</b> 23 March 2000 (23.03.00)
<b>(21) International Application Number:</b> PCT/US99/21174 <b>(22) International Filing Date:</b> 13 September 1999 (13.09.99) <b>(30) Priority Data:</b> 60/100,078 14 September 1998 (14.09.98) US <b>(71) Applicant (for all designated States except US):</b> DIAMOND MATERIALS INC. [US/US]; 120 Centennial Avenue, Piscataway, NJ 08854-3908 (US). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> VORONOV, Oleg, A. [RU/US]; 56B Cedar Lane, Highland Park, NJ 08904 (US). TOMPA, Gary, S. [US/US]; 43 Franklin Drive, Belle Mead, NJ 08502 (US). <b>(74) Agent:</b> BOTJER, William, L.; P.O. Box 478, Center Moriches, NY 11934 (US).		<b>(81) Designated States:</b> JP, KR, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). <b>Published</b> <i>With international search report.</i> <b>(88) Date of publication of the international search report:</b> 25 May 2000 (25.05.00)
<b>(54) Title:</b> FULLERENE BASED SINTERED CARBON MATERIALS <b>(57) Abstract</b> <p>A new class of carbon materials and their synthesis. The new carbon materials are formed by high pressure and high temperature processing of fullerene based carbon powder. The new carbon materials are harder than graphite and can be harder than steel (when the starting fullerenes are single wall nanotubes) or almost as hard as diamond (when the starting fullerenes are C<sub>60</sub> buckyballs). The physical attributes of the materials can also be controlled by the pressing and heating parameters. These new carbon materials are conductive like graphite and unlike diamond which is an insulator. The materials can be formed by powder metallurgy techniques into any shape (cylinders, balls, tubes, rods, cones, foils, fibers or others). The new materials can also be readily doped, converted to diamond, formed within a porous composite or converted to diamond within the porous composite.</p>		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav	TM	Turkmenistan
BF	Burkina Faso	GR	Greece		Republic of Macedonia	TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's	NZ	New Zealand		
CM	Cameroon		Republic of Korea	PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakhstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US99/21174**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(6) :C01B 31/02, 31/06; B01J 3/06

US CL :423/445B, 446, 445R

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 423/445B, 446, 445R

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CAS ONLINE: search terms GPa, gigapascal, fullerene, C60

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ----	KOZLOV, M.E., et al. Transformation of C60 Fullerenes into a Superhard Form of Carbon at Moderate Pressure. Applied Physics Letters, 06 March 1995, Vol. 66, # 10, pages 1199-1201, especially page 1200.	1-2,4-8,10,16-17,19
Y		----- 11-13
Y	Ma, Y., et al. Conversion of Fullerenes to Diamond Under High Pressure and High Temperature. Applied Physics Letters, 15 August 1994, Vol. 65, # 7, pages 822-823.	11-13
X	ZHANG, M. et al. Thermal Stability of Carbon Nanotubes under 5.5 GPa. Carbon, September 1997, Vol. 35, #10-11, pages 1671-1673.	1,3,8,9,17,18

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*E* earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A* document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means	
*P* document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

30 NOVEMBER 1999

Date of mailing of the international search report

22 DEC 1999

Name and mailing address of the ISA/US  
Commissioner of Patents and Trademarks  
Box PCT  
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

PETER DIMAURO

Telephone No. (703) 308-0651